Modelling of Na-Ion Conductors

Project Manager
David Kasdorf

Principal Investigator
Prof. Dr. rer. nat. Karsten Albe

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Clusters
Lichtenberg Cluster Darmstadt

Software
VASP, Ovito

Additional Software
VESTA

Institute
Materials Science

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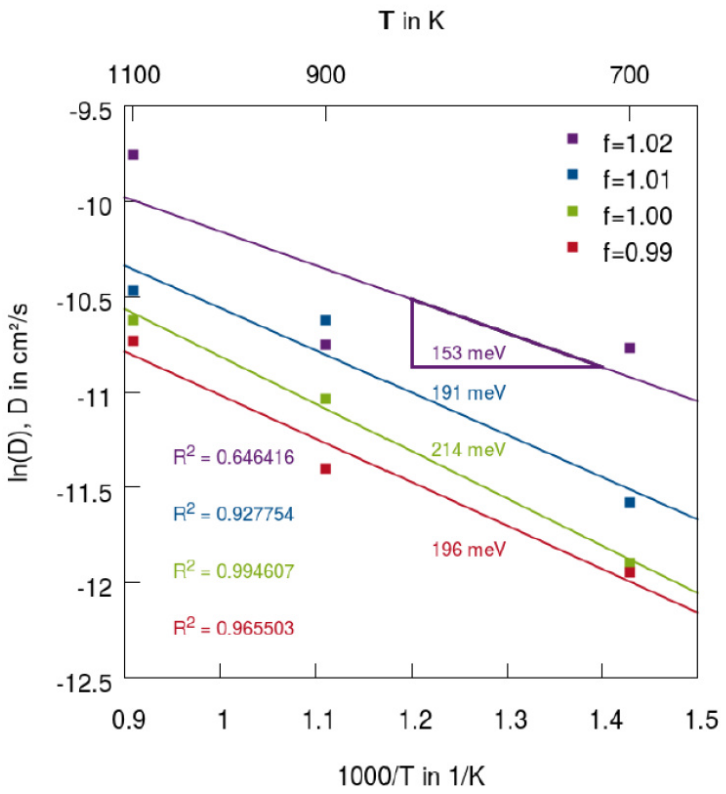


Figure 1: Arrhenius-plot of the Na^+ tracer diffusion at different volumes and temperatures.

Introduction

NASICON, short for Na^+ Superionic Conductor, is a group of materials with the composition $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ with $0 < x < 3$. As the name suggests, it is a material with a possible application in Na-ion batteries. In contrast to batteries that rely on a Li chemistry, Na and its salts are much more abundant and therefore inexpensive. The main disadvantage of this type of electrolyte is the low ionic conductivity [1]. For this reason most Na-based batteries that are in use today are thermal batteries - a type of battery that is only active when a certain temperature, and with it a required ionic conductivity, is reached. Ab initio molecular dynamics (AIMD) simulations based on Density Functional Theory (DFT) are carried out in order to investigate the Na-ion conductivity and the respective diffusion pathways. Since this method relies on a multitude of comparatively complex DFT force and energy calculations, HPC resources are necessary to compute simulations of relevant scale and time.

Methods

DFT relaxations and AIMD simulations have been carried out with the Vienna ab initio simulation package (VASP) using

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projector augmented-wave (PAW) pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Cells containing 6 formula units of $Na_3Zr_2Si_2PO_{12}$ were relaxed with a 2×2×□1 k-points mesh, a plane wave energy cutoff of 600 eV until the energy difference between two steps of electronic relaxation was smaller than 10^{-6} eV and the the residual forces between ions were smaller than 0.01 eV $Å^{-1}$. AIMD simulation were set up as canonical ensembles with temperatures of 700 K, 900K and 1100K for 2×2×□1 supercells (480 atoms). Only the G-point, the standard plane-wave cutoff energy from the pseudopotentials and an electronic convergence criterion for energy differences of 10^{-5} eV were used in order to reach longer simulation times. The time steps were set to 2 fs. We investigated cells of different volumes, which are here described by their linear scaling factor ƒ. The fully relaxed cell is named ƒ = 1.00, while the volume of other cells was set to ƒ = 0.99, ƒ = 1.01 and ƒ = 1.02. The volume with respect to the scaling factor is then $V_ƒ = ƒ^3$ □$V_ƒ$ =1.00.

Results

We investigated the mean squared displacement (MSD) of Na-ions in $Na_3Zr_2Si_2PO_{12}$ supercells of different volume at the temperatures 700 K, 900K and 1100 K. The slope of the MSD, which is equivalent to a tracer diffusion coefficient, are then collected as data points in an Arrheniusplot (see Figure 1). The slope of data points from one volume then gives the mean activation energy (indicated by the triangle in Figure 1) for diffusion processes while the y-intercept yields the pre-exponential factors D_0.

Discussion

The degree of dilatation seems to almost exclusively influence the activation barrier Ea. In case of the dilated structures (ƒ > 1.00) it can be concluded that diffusion pathways and especially their bottlenecks widen up which leads to a direct increase in ion conductivity. Interestingly, the compressed structure ƒ=0.99 also shows lower activation barriers. The overall tracer diffusion of this structure is still the lowest because of the inferior pre-exponential factor D_0. Instead artificially dilating the structure, NASICON with the addition of bigger dopants can be investigated in the future. This could open up the diffusion pathways and, as our study suggests, increase the Na-ion conductivity even at lower temperatures. Cheap, room temperature Na-ion batteries could be used where Li-ion batteries are too expensive or unsafe, e.g. large-scale energy storage.

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